

United States Patent Application for

SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES

Inventors: **SUDIPTA SEAL**
SATYAJIT SHUKLA

for the University of Central Florida

Attorney's Docket No. UCF-374

I certify that this correspondence, including the attachments listed, is being deposited with the United States Postal Service, Express Mail Post Office to Addressee service, receipt No. EV326214868US, in an envelope addressed to Commissioner of Patents, MAIL STOP Patent Applications, P.O. Box 1450, Alexandria, VA 22313-1450.

~~10/10/03~~
Date of Mailing

Signature of Person Mailing

SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES

This invention claims the benefit of priority from U.S. Provisional application

5 60/408,325 filed September 5, 2002, and was supported in part by National Science
Foundation (NSF) Grant # EEC:0136710.

FIELD OF INVENTION

This invention relates to nanoparticles and more particular to monodispersed,
10 spherical ZrO₂ particles in the size range of approximately 10 to approximately 600 nm.
exhibiting metastable tetragonal crystal structure at room temperature and this invention
provides the synthesis, for the first time, using the sol-gel technique and without doping
any trivalent impurities, of monodispersed, spherical ZrO₂ particles in the size range of
approximately 10 to approximately 600 nm, exhibiting metastable tetragonal crystal
15 structure at room temperature. This invention has revealed using high-resolution
transmission electron microscopy that “hard-aggregates” forming tendency of ZrO₂
nanocrystallites of size approximately 30 to approximately 45 nm is responsible for
stabilizing the high-temperature metastable tetragonal phase, at room temperature within
large sized (500-600) undoped ZrO₂ particles.

20

BACKGROUND AND PRIOR ART

Zirconium (ZrO₂) is a well-known structural ceramic, which exhibits tetragonal-to-monoclinic martensitic phase transformation. This phase transformation is of technological importance as it contributes to the toughening of ceramics. Porter, D.L.,

Evans, A.G., Heuer, A. H., *Acta Metall.*, 1979, 27, 1649. The tetragonal-to-monoclinic phase transformation is accompanied by volume expansion and can be triggered by hydrostatic and shear stresses. See Simha, N., Truskinovsky, L. *Acta Metall. Mater.* 1994, 42, 3827.

5 This type of transformation can take place near the crack tip due to local stress concentration, which can blunt the crack tip as a result of the development of compressive stresses associated with the phase transformation; thus, delaying the crack propagation and resisting subsequent fracture.

Zirconia is used as a dispersed phase in oxide (alumina) (Kosmac, T, Swain, 10 M.V. Claussen, N, *Mater. Sci Eng.* 1984, 71,57). as well as non-oxide (carbides, borides, and nitrides) (Swain, M.V. *Mater. Forum* 1988, 11, 182.) ceramics to increase their fracture toughness, strength, and hardness. This stress induced transformation has also been shown to increase the plasticity from the shape deformation and accommodation strains, which are associated with the transformation. (Muddle, B. C. 15 Kelly, P.M. *MaterForum* 1988, 11, 182.) Increase in the wear and corrosion resistance of nanostructured ceramic coatings as a result of stress-induced phase transformation has also been reported. (Aita, C.R., In *Advances in Catings: TMS Annual Meeting*, Warrendale, PA, 1995 p. 235) Besides this, tetragonal ZrO₂ also finds application as catalyst/catalyst support for various gas-phase reactions. (Haruta, M. Kobayashi, T, Sano, 20 H., Yamada, N *Chem Lett.* 1987, 829, 405 and Knell, A, Barnickel, P, Baiker, A, Wokaum, A. *J. Catal.* 1992, 137, 306.) Hence, synthesizing ZrO₂ particles with metastable tetragonal crystal structure is important.

Doping zirconia with trivalent impurities has been a traditional approach for the metastable tetragonal phase stabilization. (Ping, L, Chen, L.W., Penner-Hahn, J.E., J. Am Ceram Soc. 1994, 77, 188.) Particle size has also been observed to have its own effect on the metastable tetragonal phase stability in nanocrystalline zirconia. (Garvie, R. C., J. 5 Phys. Chem 1965, 69, 1238, and Nitsche, R, Rodewald, M, Skandan, G, Guess, H., Hahn, H. Nanostruct. Mater. 1996, 7, 535, and Nitsche, R, Winterer, M, Hahn, H, Nanostruct. Mater. 1995, 6, 1979). Due to the existence of a critical nanoparticle size for the metastable tetragonal phase stabilization, the tetragonal phase stabilization within the submicron sized ZrO_2 particles has been unachievable.

10

SUMMARY OF THE INVENTION

The first objective of this invention is to provide ultra fine approximately 10 to approximately 600 nm and more particularly approximately 10 to approximately 30 nm and sub-micron sized (approximately 500 to approximately 600 nm) ZrO_2 nanoparticles that are in the metastable tetragonal phase.

15

The second objective of this invention is to provide a method for synthesizing particles of the size range of approximately 10 to approximately 600 nm and more particularly nano (approximately 10 to approximately 30 nm) and sub micron (approximately 500 to approximately 600 nm) ZrO_2 nanoparticles in the metastable tetragonal phase.

20

The third objective is to provide coatings of ZrO_2 coatings on metal substrates. A preferred embodiment of the invention includes monodispersed, spherical zirconia (ZrO_2) particles of approximately 10 to approximately 600 nm, which exhibit

metastable tetragonal crystal structure at room temperature. The ZrO₂ particles are approximately 100% in the tetragonal phase at room temperature, and the particles are pure and free of foreign oxides.

A preferred method for the synthesis of monodispersed, spherical ZrO₂ particles, 5 which exhibit approximately 100% metastable tetragonal structure at room temperature, of sizes of approximately 10 to approximately 600 nm, in powder form can include various steps. The initial step can include mixing zirconium-alkoxide and an alcohol, forming preparation one, followed by separately dissolving completely de-ionized water and a polymeric steric stabilizer in an alcohol forming preparation two. Next the 10 preparation one and the preparation two can be mixed with vigorous stirring for a approximately few minutes only, subjecting the materials to hydrolysis and condensation reactions with very slow stirring. Next, there is waiting for the formation of a sol from the mixture. Next, there is drying at approximately 80 degrees C to form resultant material followed by crushing the resultant material.

15 The polymeric steric stabilizer can be an organic polymer containing -OH or ether group. The polymeric steric stabilizer can be from one of the group consisting of hydroxypropyl cellulose polymer (HPC), polyvinylalcohol, ethylene glycol, and hexamethyldisilazane. The zirconium-alkoxide can be zirconium (IV) n propoxide and the alcohol can be anhydrous alcohol. Synthesis can take place under normal 20 atmospheric conditions. The polymeric steric stabilizer can be an HPC polymer, and have a molecular weight of approximately 80,000 to approximately 1,000,000.

Further objects and advantages of this invention will be apparent from the following detailed description of the presently preferred embodiments which are illustrated schematically in the accompanying drawings.

BRIEF DESCRIPTION OF THE FIGURES

5 Fig. 1a shows nanocrystalline (approximately 20 to approximately 25 nm) sized spherical ZrO_2 particles synthesized using the sol-gel technique under the processing conditions of $R = 60$ and $HPC = 1.0$ g/L.

Fig. 1b shows monodispersed, submicron sized approximately 500 to approximately 600 nm spherical ZrO_2 particles synthesized using the sol-gel technique under

10 processing conditions of $R = 5$, and $HPC = 1.0$ g/L.

Fig. 2a shows HRTEM analysis of monodispersed submicron sized spherical ZrO_2 particles synthesized under the processing conditions of $R=5$ and $HPC =1.0$ g/L after calcinations at 400 degrees for 2 hours.

15 Fig. 2b shows the SAED patterns obtained for monodispersed, submicron sized (approximately 500- approximately 600 nm) spherical ZrO_2 particles at the edge of a particle after calcination at 400 degrees C for 2 hours.

Fig. 2c shows SAED patterns obtained for monodispersed submicron sized (approximately 500 to approximately 600nm) spherical ZrO_2 particles at the center of a particle after calcinations at 400 degrees C for 2 hours.

20 Fig. 3 shows typical broad scan XRD patterns, within 20 range of 10 degrees to 80 degrees, obtained for nanocrystalline ZrO_2 particles of size approximately 20 to approximately 25 nm after calcinations at 400 degrees C for 2 hours, synthesized under the processing conditions of $R =60$, and $HPC = 1.0$ g/L.

Fig. 4 shows typical broad scan XRD patterns, within 2ι range of approximately 10° to approximately 80° , obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles, after calcination at 400°C for 2 h, synthesized under the processing conditions of $R = 5$, and $\text{HPC}=1.0 \text{ g/L}$.

5 Fig. 5 shows typical narrow scan XRD patterns obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles, after calcination at higher temperatures for 2 h, synthesized under the processing conditions of $R = 5$, and $\text{HPC}=1.0 \text{ g/L}$.

10 Fig. 6a provides schematic diagrams showing the ZrO_2 nanocrystallites forming loose-aggregates.

Fig 6b provides schematic diagram showing the ZrO_2 nanocrystallites forming hard-aggregates.

15 Fig 6c provides a schematic representation of the athermal nature of tetragonal to monoclinic phase transformation in nanocrystalline ZrO_2 . The calcination temperature increases from (i) to (iii) represents the temperature range of $400\text{-}800^\circ\text{C}$.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before explaining the disclosed embodiments of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangements shown since the invention is capable of other embodiments.

20 Also, the terminology used herein is for the purpose of description and not of limitation.

This invention demonstrates for the first time that, at room temperature, the stability of the metastable tetragonal phase within the submicron sized ZrO_2 particles

strongly depends on the aggregation tendency of ZrO_2 nanocrystallites. As a result of strong aggregation of ZrO_2 nanocrystallites, the inventors have been able to synthesize both nano (approximately 10 to approximately 30 nm) and large sized (approximately 500 to approximately 600 nm) ZrO_2 particles having 100% tetragonal crystal structure.

5 This particle size is much larger than the critical size of approximately 6 nm, reported in the prior art, for the stabilization of 100% tetragonal phase.

To prepare the nanoparticles of the invention, pure zirconium(IV) n-propoxide anhydrous ethanol (approximately 200 proof) and the HPC polymer (hydroxypropylcellulose, molecular weight approximately 80,000 g/mol) used as a 10 polymeric steric stabilizer were obtained from Aldrich Co and were used as received

Other alcohols and zirconium alkoxides may also be used. Other polymeric steric stabilizers may also be used such as any compound with -OH or ether groups, for example polyvinylalcohol, ethylene glycol, or hexamethyldisilazane .

Other ceramic oxides can be used in addition to zirconium, for example, tin, 15 indium, and titanium.

Nanocrystalline ZrO_2 powder is synthesized by hydrolysis of zirconium (IV) n-propoxide in an alcohol solution. The beakers used in the experiments were cleaned, washed with deionizer water, dried completely and rinsed with anhydrous 200 proof ethanol. During synthesis, two different but equal parts of alcohol solutions were 20 prepared. In the first part, deionized water was dissolved into anhydrous 200 proof ethanol using two different R values (R)=5 and 60, which is the ratio of molar concentration of water to zirconium(IV) n-propoxide. HPC polymer (HPC) =1.0 g/L was then added to this part and was dissolved completely by stirring the solution overnight

using a magnetic stirrer. The second part of the alcohol solution was then prepared by completely dissolving zirconium (IV) *n*-propoxide (0.1 M) in anhydrous 200 proof ethanol under normal atmospheric conditions and homogenized using magnetic stirring for a few minutes only. After preparing each solution, both the beakers were sealed 5 immediately with paraffin tape. Hydrolysis of zirconium(IV) *n*-propoxide was then carried out under atmospheric conditions by rapidly mixing the two sealed solutions under vigorous stirring. The formation of ZrO₂ particles was evident from the white color of the resulting sol due to immediate precipitation.

The sol was stirred very slowly for approximately 4 hours and then held under 10 static conditions for 24 h to ensure completion of the hydrolysis and condensation reactions. The sol was subsequently dried at approximately 80°C using Petri dishes in order to remove the solvent completely. The small gel pieces obtained were then crushed to obtain the nanocrystalline ZrO₂ powder, which was calcined at different temperatures ranging from approximately 400° to approximately 800°C in air for the phase evolution 15 study. The samples were heated at a rate of approximately 30°C/min up to the calcination temperature, held at that temperature for 2 hours, and then slowly cooled to room temperature in the furnace. The as-synthesized nanocrystalline ZrO₂ powders were then examined using a Phillips EM400 transmission electron microscope (TEM) at 120 kV. A high-resolution field TEM (HRTEM) (FEI-Philips Tecnai F30) was used to 20 observe lattice images showing different orientations of nanocrystals within a submicron sized ZrO₂ particle, after calcination at approximately 400°C for 2 h.. Bright field TEM images at 300 kV were taken to observe the lattice. Selected-area electron diffraction (SAED) patterns were taken to analyze the crystal structure. SAED patterns collected

near the edge and from the center of the particle, provided the presence of nanocrystals within a submicron sized particle.

The crystalline phases present in the as-synthesized and calcined powders were also determined using a standard Rigaku X-ray diffractometer (XRD). Line traces were 5 obtained over 2ι values ranging from approximately 10° to approximately 80° . Narrow scan analysis was conducted in the 2ι range of approximately 29.5° to approximately 31.5° , as it contained the strongest line for the tetragonal (111)t phase. This intense peak was then curve fitted using the peak-fit software (peak-fit, version-4, SPSS Inc.). The average tetragonal crystallite size (D_t) was calculated from the (111)t diffraction peak 10 using Scherrer's equation, where, D is the average crystallite size in nm, λ is the radiation wavelength (approximately 0.154 nm), β' is the corrected halfwidth at half-intensity (fwhm) and ι is the diffraction peak angle.

TEM images of nanocrystalline and submicron sized ZrO_2 particles synthesized via the sol-gel technique, under the processing conditions of R) 60 and R) 5, at 15 [HPC]g/L, are shown in Figures 1a and 1b, respectively. ZrO_2 nanocrystallites of size approximately 20 to approximately 25 nm are synthesized under the processing conditions of R) 60, [HPC]) approximately 1.0 g/L, Figure 1a. ZrO_2 nanocrystallites form "loose-agglomerates" under these processing conditions. On the other hand, 20 monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles are formed under the synthesis conditions of R) 5, [HPC]) 1.0 g/L, Figure 1b. An HRTEM image obtained from the edge of one of the ZrO_2 particle, Figure 1b, after annealing at 400°C for 2 h, is shown in Figure 2a.

Two tetragonal lattices are observed in Figure 2a having different relative orientations. SAED images obtained from the edge and the center of ZrO₂ particle, Figure 1b, after annealing at approximately 400 °C for 2 h, are shown in Figures 2b and 2c, respectively. More diffraction spots are observed in the SAED pattern obtained from the center of the ZrO₂ particle, Figure 2c, than are obtained from the edge of the particle, Figure 2b. In fact, we observed a gradual increase in the number of diffraction spots when traversed from the edge toward the center of the particle. This indicates that a larger number of nanocrystallites are located at the center of the particle than that at the particle edge. Typical broad-scan XRD patterns obtained for ZrO₂ particles synthesized under the two different processing conditions, Figure 1a, 1b are presented in Figures 3 and 4 respectively, as a function of calcination temperature. The as-synthesized ZrO₂ particles are observed to be X-ray amorphous; however, they crystallize at the calcinations temperature of approximately 400 degrees C. ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm exhibit tetragonal and monoclinic crystal structure after calcinations at approximately 400 degrees C for 2 h, as shown in Figure 3.

Tetragonal-to-monoclinic phase transformation is observed at approximately 600 degrees C, which increases the relative volume fraction of monoclinic phase at the expense of the tetragonal phase. The phase transformation almost goes to completion after calcinations at approximately 800 degrees C.

Thus, gradual transformation of tetragonal phase to monoclinic phase is observed for ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm with increasing calcinations temperature within the range of approximately 400 to approximately 800 degrees C. On the other hand, monodispersed, submicron sized

(approximately 500 to approximately 600 nm) spherical ZrO_2 particles do not exhibit gradual phase transformation as a function of increasing calcination temperature, Figure 4. The high-temperature metastable tetragonal phase is observed to nucleate from the amorphous phase at approximately 400°C and is also observed to be stable after 5 calcination at approximately 600°C. No monoclinic phase is detected at the calcination temperatures of approximately 400°C and approximately 600°C. However, when calcined at approximately 800°C, almost complete tetragonal to monoclinic phase transformation is observed.

Typical narrow XRD scans of the (111)_t peak, corresponding to the tetragonal 10 phase, for monodispersed, submicron sized, spherical ZrO_2 particles, after calcination at approximately 400°C and approximately 600°C, are shown in Figures 5a and 5b, respectively. The crystallite size of approximately 45 nm is calculated using Scherrer's 15 equation (Cullity, B.D., 1978. Elements of S-Ray Diffraction, Addison-Weley, Massachusetts.) for monodispersed, submicron sized, spherical ZrO_2 particles after calcination at approximately 400°C. Moreover, decrease in the FWHM is observed in Figure 5 with increase in the calcination temperature.

TEM analysis reveals that the ZrO_2 nanoparticles of size approximately 20 to 20 approximately 25 nm synthesized at large R value 60 form "loose-agglomerates" as schematically shown in Figure 6a. The formation of loose-agglomerates is due to high nucleation rates associated with large R value. By contrast, XRD and HRTEM analysis and corresponding SAED patterns obtained for monodispersed, submicron sized, spherical ZrO_2 particles, after calcination at approximately 400°C, indicate that these particles are made up of small nanocrystallites of size approximately 45 nm, as

schematically shown in Figure 6b. It appears that ZrO_2 nanocrystallites form “hard-aggregates” under the processing conditions of $R = 5$, $[\text{HPC}] = 1.0 \text{ g/L}$, due to very slow kinetics of hydrolysis and condensation reactions associated with low R value.

The submicron sized ZrO_2 particles of size approximately 500 to approximately 5 600 nm are expected to exhibit monoclinic crystal structure at room temperature, as the particle size is much greater than the critical size of approximately 6 nm to have any thermodynamic effect for high-temperature metastable tetragonal phase stabilization. The tendency of the ZrO_2 nanocrystallites to form hard-aggregates and loose-10 agglomerates is, however, observed to significantly affect its phase transformation behavior at higher temperatures.

The temperature of metastable tetragonal polymorph of ZrO_2 is stabilized at room temperature within the monodispersed submicron sized (approximately 500 to approximately 600 nm) spherical ZrO_2 particles without doping any trivalent impurity. Various theories have been proposed for the stabilization of metastable tetragonal phase15 in nanocrystalline ZrO_2 at room temperature.

Garvie,(R.C. J Phy. chem, 1965, 69, 1238) experimentally (using XRD) and using thermodynamic calculations, showed the existence of a critical size of 20 nm, below which the metastable tetragonal phase is stable in nanocrystalline ZrO_2 and above which the monoclinic phase is stable. Mitsuhashi et al.,(J. Am. Ceram. Soc. 1974, 57, 20 97) however, showed that the metastable tetragonal phase can be stabilized in ZrO_2 nanocrystallites of size greater than approximately 30 nm due to the strain energy involved at the interphase boundaries resulting from the simultaneous presence of monoclinic and tetragonal phases within the crystallites. By HRTEM analysis Nitsche et

al further showed that the critical size for 100% tetragonal phase stabilization in nanocrystalline ZrO_2 is about 6 nm, above which ZrO_2 nanocrystallites exist as a core-shell particles with tetragonal phase, as a core and monoclinic phase as a shell. In our invention, ZrO_2 nanocrystallites of size as small as about 20 to about 25 nm are 5 synthesized (Figure 1a) which are larger than the critical size of about 6 nm for the stabilization of the about 100% tetragonal phase. This is probably the reason for the appearance of tetragonal as well as monoclinic phases when these ZrO_2 nanocrystallites are calcined at the crystallization temperature of 400 degrees C. With increased calcinations temperature above 400 degrees C, the phase transformation possibly 10 proceeds in a manner as described schematically in Figure 6c.

The tetragonal-to-monoclinic phase transformation in ZrO_2 is athermal in nature. As a result, a specific amount of monoclinic phase is formed at each calcination temperature, as observed in Figure 3. As mentioned earlier, monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles are 15 composed of small nanocrystallites of size approximately 45 nm after calcination at 400°C. The nanocrystallite size of approximately 45 nm is also larger than the predicted and observed critical size of approximately 30 nm¹⁰ and approximately 6 nm^{11,12} respectively for approximately 100% metastable tetragonal phase stabilization. However, interestingly, no monoclinic phase formation is observed after crystallization of 20 submicron sized ZrO_2 particles at 400°C, Figure 4.

Moreover, the nanocrystallites within the submicron sized ZrO_2 particles are observed to grow due to calcination at 600°C, which is indicated by the decrease in the FWHM of the (111)_t peak with increase in the calcination temperature. Even after the

growth of the nanocrystallites above approximately 45 nm size, no tetragonal to monoclinic phase transformation is observed at approximately 600°C. Hence, the tetragonal-to-monoclinic phase transformation appears to be suppressed within the submicron sized ZrO₂ particles at 600°C. Thus, the phase evolution behavior exhibited 5 by the monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles is in contrast with that of ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm.

It is noted that ZrO₂ nanocrystallites (approximately 45 nm) form hard-aggregates of size approximately 500 to approximately 600 nm, under the processing conditions of R 10 5, [HPC]) 1.0 g/L, while ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm, synthesized under the processing conditions of R) 60, [HPC]) 1.0 g/L, form loose-agglomerates. It appears that due to the formation of hard-aggregates, the tetragonal-to-monoclinic phase transformation, which is accompanied by volume expansion, is suppressed at approximately 400°C and approximately 600°C. As a result, 15 monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles having metastable tetragonal crystal structure are successfully synthesized in the present investigation.

The stabilization of metastable of tetragonal phase via proposed mechanism, which involves the suppression of volume increase associated with the tetragonal-to- 20 monoclinic phase transformation, due to dense agglomeration of nanocrystallites within monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles, is supported by the following observations. First, the volume expansion associated with the tetragonal to monoclinic phase transformation would cause many

stresses and strains to be included in the structure that might lead to fracture of the particles. However, no such type of fracture of monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles has been observed, which supports the stabilization of tetragonal phase in the large sized particles.

5 Second, there is substantial evidence (obtained via HRTEM) of little or no free volume in the monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles. Analogous to the glass transition in polymers, if there were free volume in these large particles, this excess free volume would permit the phase transition to take place. Finally, considering the precursors involved during the sol gel synthesis of

10 ZrO₂ particles, there is no evidence of any group III impurity that might be otherwise stabilizing the tetragonal phase.

Nanosized (approximately 20 to approximately 25 nm) and submicron sized (approximately 500 to approximately 600 nm), monodispersed, spherical ZrO₂ particles are successfully synthesized using the sol-gel technique. The tendency of ZrO₂

15 nanocrystallites (approximately 45 nm) to form hard-aggregates is observed to be responsible for the high-temperature metastable tetragonal phase stabilization, at room temperature, within the submicron sized ZrO₂ particles.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice,

20 the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.